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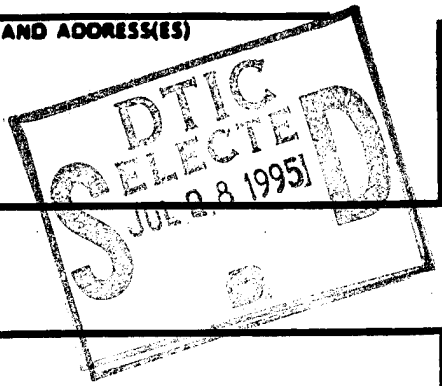

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This report describes development of the chemistry and applications of a new biomimetic in situ synthetic system for the fabrication of inorganic/organic composite materials. The major findings involve understanding the mechanisms of the solid-state syntheses which give rise to composites in which the crystals of the inorganic phase are identical in size, morphology, and crystallographic orientation, the determing charateristics of naturally-formed biological composites. Synthetic control over the morphology and therefore of the material properties of both the organic and inorganicphases of these new materials, as well as the mixing of the two disparate phases on the molecular level, is found to be affected primarily by 1) general factors controlling the crystallization of CdS in polymers, 2) surfactant effects on crystal growth and organization, and 3) matrix effects on crystal growth and organization.

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Abstract

AFOSR Grant No.: F49620-92-J-0296

Title: Fabrication of Biomimetic Molecular Level Composites

Period: 01 Jun 94 - 31 May 95

Principal Investigator: Patricia A. Bianconi
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This report describes development of the chemistry and applications of a new biomimetic in situ synthetic system for the fabrication of inorganic/organic composite materials. The major findings involve understanding the mechanisms of the solid-state syntheses which give rise to composites in which the crystals of the inorganic phase are identical in size, morphology, and crystallographic orientation, the determing charateristics of naturally-formed biological composites. Synthetic control over the morphology and therefore of the material properties of both the organic and inorganic phases of these new materials, as well as the mixing of the two disparate phases on the molecular level, is found to be affected primarily by 1) general factors controlling the crystallization of CdS in polymers, 2) surfactant effects on crystal growth and organization, and 3) matrix effects on crystal growth and organization.

FINAL TECHNICAL REPORT

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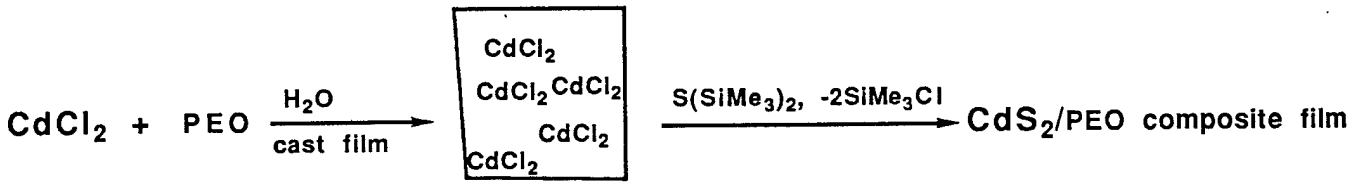
Biological composite materials such as bones, teeth, and shells, consist of a polymeric matrix reinforced by an inorganic phase which forms within the matrix. These materials are distinguished from synthetic composites by the high degree of organization and regularity displayed by the inorganic phase. Inorganic minerals of uniform size, morphology, and crystallographic orientation can be formed in ordered arrays within living cells. Such a process has not been realized in synthetic systems, although recent strong interest in nanoscience has stimulated much research in the area. We have reported an example of a synthetic process which produces composite materials analogous to those produced by natural biomineralization. The inorganic/organic in-situ synthesized composites display controlled inorganic crystal size, morphology, and orientation, which characteristics are determining features of Type II, or matrix-mediated, biocomposites. The synthetic factors which we attempted to optimize in order to give biomimetic properties to synthetic composites were 1) strong binding by the organic matrix of the inorganic reagents (molecular complementarity), 2) good "solvation" of the inorganic reagents by the polymer, and 3) an ordered, regular polymer environment in which to induce nucleation (matrix preorganization). In this work we have studied the ordered crystallization process in greater detail and attempted to analyze the ways by which some of the variable synthetic factors present in this system affect the organization of the polymer-grown crystals obtained. Application of these factors may allow the fabrication of synthetic materials with the control, order, and regularity of biominerals, and open many opportunities for accessing unique materials and properties.

This research has been carried out by one graduate student, Elizabeth Cates, who was supported by research assistantships during the summer and the academic year and whose laboratory expenditures were supported. The crystallization system most studied was that of CdS formed in situ in a poly(ethyleneoxide) (PEO) polymer film, as shown in Scheme I:



polymer film containing inorganic reagent

Scheme I

Our principal findings are in three areas, in each of which a manuscript is in print or in preparation. These areas are 1) general factors controlling the crystallization of CdS in polymers, 2) surfactant effects on crystal growth and organization, and 3) matrix effects on crystal growth and organization.

General Factors Controlling Crystallization in Polymers

One of the most important effects exerted by the polymer crystallization matrix is the "solid state" effect, or that, in order to obtain significant matrix mediation, the polymer must be a dense solid. Any sort of solvation or relaxation of the matrix results in loss of control over crystallization. For example, when THF or any solvent capable of dissolving or swelling the PEO matrix is used as the reaction medium (or "carrier solvent") in the reaction shown in Scheme I, significant amounts of Cd diffuse out of the polymer, forming CdS in solution. Also, in such reactions no crystallization control is seen: amorphous CdS in irregular shapes results. Identical reactions in octane, an inert solvent for PEO, produce no loss of Cd from the polymer, and result in more regular and crystalline CdS. These results imply that the crystallization occurs within the polymer matrix, not on the surface with the polymer acting solely as a template (a model that had previously been suggested), and suggest that such a crystallization mechanism may also be important in biological minerlaization systems. A second effect exerted by the polymer matrix which was demonstrated to be necessary for control of crystallization is strong binding of the inorganic reagents by the matrix on a molecular level. This effect controls the homogeneous dispersion of the inorganic phase and also the molecular-level structural modifications which are seen in biological systems. Experiments using non-binding polymer matrices (poly[methylmethacrylate] and poly[styrene]) give phase-separated inorganic /organic composites,

with the inorganic phase often forming a network on the surface of the film. When a copolymer containing both binding and non-binding groups (70:30 poly[2-vinylpyridine]-co-poly[styrene]) is used as a crystallization matrix, the CdS is homogeneously dispersedthroughout the film in isolated particles organized into the binding regions. No surface inorganic layer is formed. Analogous results were obtained when HgS was synthesized in polymer films containing binding and non-binding groups in a manner similar to that shown in Scheme I, using $HgPh_2$ as the inorganic reagent. That molecular level dispersion of the inorganic regents is necessary to matrix-mediation of their reaction products was demonstrated by the in-situ synthesis of PbS in PEO. The inorganic reagent chosen for this synthesis was $PbCl_2$, specifically because, unlike $CdCl_2$ and $HgPh_2$, it does not "dissolve" in the polymer matrix, but rather forms nanometer-sized crystalline aggregates which can be observed by electron microscopy and xray diffraction. The resulting PbS was found to be formed in similar nanometer-sized aggregate crystals, with no structural mediation by the matrix; addition of the surfactant AOT (see below) did not alter this result. These results demonstrate that molecular-level solvation and binding by the polymer matrix is required for any molecular-level matrix-mediation of in-situ reactions.

Our experiments have virtually ruled out.a previously proposed crystallization mechanism--that rock salt CdS is formed under a thin template crystal of NaCl, formed on the polymer surface during the reaction shown in Scheme I. No NaCl has been seen in the films by any spectroscopic technique; its absence is attributed to the excellent chloride-scavenging abiity of the silicon reagent used and the high solubility of NaCl in PEO, which would prevent crystal formation. Also, we have now synthesized crystallographically oriented CdS in the zinc blende structure by the in situ method (see below), a structure which NaCl cannot adopt and therefore cannot template. This template mechanism could possibly be realized by using a weaker silicon-binding halide ion (for example, Br^-) or forming a less soluble alkali metal halide (for example, KBr rather than NaCl). Research into realization of this crystallization mechanism continues. Finally, our results show that a crystalline polymer matrix, while indeed necessary for the production of regularly-shaped crystals by the vectorial aggregation of amorphous particles, may not be needed for the synthesis

of organized arrays of single crystals, as was previously thought. Matrix-mediation by other mechanisms (see below) is now thought to be the primary means by which organized crystals are synthesized, and the crystallinity or regularity of the matrix environment appears to be less influential. A paper reporting these results has been published (Lin, J.; Cates, E.; Bianconi, P. A., "A Synthetic Analogue of the Biomineralization Process: Controlled Crystallization of an Inorganic Phase by a Polymer Matrix", *J. Am. Chem. Soc.* **1994**, *116*, 4738-4745).

Surfactant Effects on Crystal Growth and Organization

Our experiments demonstrate that the ligands added to the in situ crystallization reaction (the surfactant AOT, sodium bis(diethylsulfosuccinate), in Scheme I) are almost solely responsible for the nucleation and orientation of of the CdS crystals. First, we have shown by xray photoelectron spectroscopy that the surfactant does indeed form a mono- or multilayer assembly on the polymer film's surface, as was previously hypothesized. That this is a surface monolayer, and that AOT is not incorporated into the bulk film, was shown by the failure of films which are cast from an AOT solution, rather than previously cast and subsequently exposed to AOT, to crystallize CdS. We have shown that this surface AOT interacts with the polymer-bound $CdCl_2$ on a molecular level: the normal crystalline diffraction pattern of the $CdCl_2$/PEO complexes formed in a solution-cast PEO film vanish when that film is subsequently exposed to AOT. The AOT therefore is binding or interacting with the polymer-bound Cd, altering its former crystalline structure. A new diffraction pattern is observed in the $CdCl_2$/PEO films when they are exposed to AOT; this could arise from formation of AOT/$CdCl_2$ crystalline structures, or from the arrangement of surface AOT in a new crystalline lattice structure when it forms layers on the PEO surface. Experiments which will distinguish between these two possibiities are now in progress. We have also shown that little or no nucleation of CdS crystals in PEO films is seen without added AOT, even in films of optimum thickness (see below). Virtually without exception, <u>all</u> single crystals of CdS obtained with AOT in these syntheses, of whatever crystalline phase, are oriented on 001: these data demonstrate that the surfactant is primarily responsible for both crystal nucleation and crystallographic orientation. 001 is the crystallographic orientation most commonly seen in

biological systems, another feature which our synthetic system has successfully imitated. Since both the zinc blende and the rock salt structures of CdS (the phases we have seen as 001-oriented single crystals) present Cd-rich faces in this orientation, our data suggests that the binding of the sulfonate headgroup to polymer-bound Cd selects the orientation of the resulting crystal. Other surfactants we have examined have proved to be too insoluble in octane to use in the current synthetic reaction. Use of a surfactant with a carboxylic acid headgroup (arachidic acid), has not produced the same nucleation/orientation as did AOT. This is attributed to the weaker binding of the headgroup to the soft Cd^{+2} ions. Arachidic acid induces mineralization in charateristic morphologies very different than those seen with AOT, thereby demonstrating the importance of the surfactant in mediating mineralization We have also shown that, contrary to what has been seen in crystallizations from solution under Langmuir-Blodgett monolayers, the surfactant in these syntheses does not determine the phase of the crystals produced. Under varying synthetic conditions (see below), we have produced both the zinc blende and rock salt phases of CdS with AOT. Crystal phase selection by lattice matching of the crystal to the interheadgroup spacing of the monolayer film is therefore not indicated.

Finally, we have demonstrated that the surfactant exerts great influence on the assembly of nucleated particles into macromolecular structures. Along with single crystals of CdS (invariably cubic or rectangular), large, very regular bipyramidal-shaped assemblies of CdS are seen in every film which has been exposed to AOT. The number of these structures increases almost linearly with increasing AOT concentration. Although perfectly regular in shape, these assemblies are not crystalline, producing only faint rings in electron diffraction studies. They appear to be formed of very small crystallites or amorphous particles assembled into regular bipyramidal shapes selected by the AOT. Upon long exposure to AOT, PEO films containing only $CdCl_2$ also form identically-shaped assemblies, demonstrating that it is the surfactant which is responsible for these assemblies and not some feature of the CdS synthetic reaction. This appears to be an example of the vectorial aggregation of amorphous or micorcrystalline particles which, in biological systems, is responsible for the formation of macroscale organized composite structures, as, for example, the spines of sea

urchins. Our current data therefore suggest that AOT nucleates crystallites by binding to polymer-bound Cd atoms near the polymer surface. At low concentrations of AOT, possibly because the polymer film has areas where there is incontinuous coverage by the surfactant monolayer, growth of single crystals may arise from these individual nucleation sites. At higher concentrations of AOT, or in regions of the film which are more completely covered by a continuous monolayer, the individual nucleation sites may assemble into regular shapes (although not yet coalescing into single crystals), the structure of which are determined by the structure of the surface monolayer. Arachidic acid also produces regular shapes, completely different than those seen with AOT. We are currently investigating by SIMS whether AOT coverage on the film's surface correlates to production of bipyramidals in these areas. Other synthetic factors (see below) also determine which sort of macromolecular crystal or assembly will arise from individual nucleation sites. We are in addition investigating methods of inducing the bipyramidal aggregates to form single crystals, as is seen in biological systems.

Matrix Effects on Crystal Growth and Organization

Our experiments demostrate that diffusion of ions or reagents within the polymer matrix is primarily responsible for regulating the morphology of the crystals or particles, for selecting whether amorphous particles, single crystals or regular assemblies will grow from particular nucleation sites, and for determining which phase single crystals will adopt. Rate of diffusion are determined, in turn, primarily by the rigidity and density of the polymer matrix: any synthetic factor which affects these features will affect the growth, morphology, and phase of the inorganic product. We have found the two most important synthetic factors which control reagent diffusion in PEO films to be the thickness of the film and its water content (water plasticizes PEO, giving the film more flexibility and therefore allowing more ion mobility within it). For example, in thinner films (approximately 50 - 100 nm), no rock salt CdS (the more dense phase) is seen; all the CdS is present as zinc blende single crystals or as irregularly-shaped amorphous aggregates. Too fast diffusion of reagents or CdS crystallites, allowed by the less dense thin film, produces more rapid assembly and therefore more uncontrolled assembly into amorphous aggregates. Those crystals

which do form adopt the zinc blende, or less dense, CdS structure. But films of the same thickness which are rigorously water-free produce rock salt crystals, as well as zinc blende. Less mobility of reagents or crystallites in the more rigid, more dense, film restricts crystal growth sufficiently for the more dense CdS phase to be favored. In thicker films (approximately 150 - 300 nm), even though their water content is higher, rock salt is the only crystalline phase observed, and irregular amorphous aggregates almost vanish. These data suggest that specific matrix properties such as film density and flexibilty determine the rate of ion or crystallite diffusion, which in turn determines the morphology and crystallinity of the CdS. Irregular, amorphous structures are produced by fast diffusion, while slower diffusion rates give rise to either Ostwald ripening of individual nucleation sites into single crystals, or assembly of individual nucleation sites into shapes determined by the structure of the AOT surface layer. In the densest films, crystal growth occurs essentially under pressure, giving rise to the rock salt or high-pressure phase. In films thicker than approximately 300 nm, no ordered crystallization (for the most part, no crystallization at all) is seen. The Cd ions within the bulk of these films have no access to the surface AOT layer, which would induce nucleation, and the films are too dense, by virtue of their thickness, to allow for a favorable diffusion rate. Our optimum film thickness range mimics that seen in biological structures: organized composites are usually composed of layers of thin organic films, 30 - 300 nm in thickness, interspersed with mineralized zones. Such biological composites never are composed of a single thick organic layer which contains organized crystals. These results suggest that, although biological composites may be organized into ubiquitous thin organic layers for a variety of reasons, one of these reasons may be that such composites must be so construcuted because thick polymer layers are physically incapable of mineralizing organized crystal arrays. We are now working on confirming these hypotheses by obtaining more precise film thickness ranges and densities, and extending these findings to other synthetic systems.

Research has been extended to the synthesis of PbS in PEO matrices. This mineral has only one reported phase, the rock salt structure. When synthesized in solution, in "thick" polymer films, or in "thin" polymer films without surfactant, mineralization is disorganinzed; no regularity

of shape or size in the PbS is seen. However, when synthesized in situ in thin films of PEO in the presence of AOT, along with some disorganized mineralization (identified by its diffraction pattern as poorly crystalline PbS), large crystals are also seen. These crystals adopt either hexagonal or tetragonal morphologies. Their diffraction patterns clearly indicate that they are not rock-salt phase PbS. However, their diffraction patterns are consistent with those reported for PbS_2 , which adopts two known phases, one hexagonal and one tetragonal. This phase is stable at atmospheric pressure, but has previously been synthesized only at 70 kbar pressure. The preferential adoption of this high-pressure phase in the biomimetic synthetic conditions is similar to that seen in actual biological systems (such as seashells, in which metastable phases of $CaCO_3$ are often found), and is consistent with the CdS results, which suggested that the density of the matrix, or the "solid-state" effect, was responsible for the preferential growth of the rock salt high-pressure phase of CdS. Further studies into the generality of the densification effect of the biomimetic synthetic system, to produce phases not usually seen at atmopheric conditions, are underway.

Publications (supported by AFOSR Grant No.F49620-92-J-0296):

1. Lin, J.; Cates, E.; Bianconi, P. A., "A Synthetic Analogue of the Biomineralization Process: Controlled Crystallization of an Inorganic Phase by a Polymer Matrix", *J. Am. Chem. Soc.* **1994**, *116*, 4738-4745.

2. Bianconi, P. A. "Biomimetic Mineralization", in Materials Chemistry: An Emerging Subdiscipline, American Chemical Society Symposium Series, 1993, in press.

3. Mark, J. E.; Lee, C. Y; Bianconi, P. A., eds., Hybrid Organic-Inorganic Composites, American Chemical Society Symposium Series, **1995**, *585*.

Manuscripts in Preparation (supported by AFOSR Grant No.F49620-92-J-0296):

1. Cates, E.; Lin, J.; Bianconi, P.A. "Controlled Crystallization of an Inorganic Phase by a Polymer Matrix: Surfactant Effects on Crystal Growth and Organization", to be submitted to *J. Am. Chem. Soc.*

2. Cates, E.; Lin, J.; Bianconi, P.A. "Controlled Crystallization of an Inorganic Phase by a Polymer Matrix: Matrix Effects on Crystal Growth and Organiczation", to be submitted to *J. Am. Chem. Soc.*

Honors and Awards (P. Bianconi):

1994-1997	DuPont Young Professor Award
1994-1996	Alfred P. Sloan Research Fellowship
1992-1997	Camille and Henry Dreyfus Teacher/Scholar Award
1992-1994	Beckman Young Investigator Award

Invited Lectures (on fabrication of biomimetic molecular level composites):

1. "Crystallization of an Inorganic Phase Controlled by a Polymer Matrix", Air Force Office of Scientific Research Workshop on Biomimetic Mineralization, Wright-Patterson Air Force Base, Dayton, OH, August 1993

2. "Crystallization of an Inorganic Phase Controlled by a Polymer Matrix", 1993 Fall Meeting of the Materials Research Society, Boston, MA, December 1993.

3. "Crystallization of an Inorganic Phase Controlled by a Polymer Matrix", J. Lin, E. Cates, and P. A. Bianconi, Beckman Foundation, Irvine, CA, August 1993

4. "Crystallization of an Inorganic Phase Controlled by a Polymer Matrix", 1994 Spring Meeting of the Materials Research Society, San Francisco, CA, April 1994.

5. "A Synthetic Analogue of the Biomineralization Process", Department of Chemistry, University of Massachusetts at Amherst, Amherst, MA, May 1995.

6. "A Synthetic Analogue of the Biomineralization Process", IV International Conference on Materials, Cancun, Mexico, August 1995.

Symposia Organized at National Meetings:

"Inorganic/Organic Polymer Composites", American Chemical Society Division of Polymeric Materials: Science and Engineering, Spring Meeting, San Diego, CA, March 13-18 1994, co-sponsors J. E. Mark and C.Y. Lee.

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1. AIR FORCE OFFICE OF SCIENTIFIC RESEARCH: "Fabrication of Biomimetic Molecular-Level Composites", July 1, 1992 - June 30, 1995, $240,000.

2. BECKMAN FOUNDATION: Beckman Young Investigator Award, "Synthetic Analogues of the Biomineralization Process", July 1, 1992 - January 1, 1995, $175,000.

3. CAMILLE AND HENRY DREYFUS FOUNDATION: Dreyfus Teacher/Scholar Award, April 14, 1992 - April 16, 1997, $50,000.

4. DEPARTMENT OF DEFENSE: "Fabrication of Biomimetic Molecular-Level Composites", Augmentation Awards for Science and Engineering Research Training, June 1, 1993 - May 31, 1996, $197,001.

5. NATIONAL SCIENCE FOUNDATION: "Functionalization of Inorganic Network Polymers", July 1, 1994 - June 30, 1997, $210,000.

6. ALFRED P. SLOAN FOUNDATION: Alfred P. Sloan Research Fellowship, September 15, 1994 - September 14, 1997, $30,000.

7. E. I. DUPONT DE NEMOURS CORPORATION: Dupont Young Professor Award, September 1, 1994 - August 31, 1997, $75,000.

8. NATIONAL SCIENCE FOUNDATION: "Research Experiences for Undergraduates at the Pennsylvania State University", June 1, 1993 - May 31, 1996, $150,000.